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STUDIES ON THE MECHANISM OF DISPERSANT ACTION: WEATHERING AND SELECTION OF ALKANES

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Introduction

Few studies have been conducted to investigate the changes in oil composition associated with chemical dispersion. Some workers have investigated the accelerated weathering or evaporation attributed to dispersant action, but did not attempt to quantify the effect. This study represents a first attempt to quantify these changes. Two specific phenomena were investigated; the accelerated weathering caused by dispersants, and secondly the change in the composition of the n-alkanes (the normal or straight-chain aliphatic compounds) which often constitute a large part of the oil's volume. These compounds are relatively easy to study by gas chromatography, being easy to identify and quantify.

The study of the compositional changes has relevance to numerous aspects of the dispersant question:

1. How do dispersants work? This question is very important because little is known about the mechanisms by which dispersants function. Most studies in the surfactant literature are related to micellization or detergency, two action mechanisms that have little relevance to oil spill dispersion. Understanding of dispersion mechanisms will greatly improve capability to improve dispersant effectiveness. Simply put, one cannot fix what one does not understand.

2. What causes effectiveness differences? The question of why similar oils with similar viscosities will sometimes display quite different dispersion, has plagued spill scientists for years. These variances were generally attributed to compositional differences, with no understanding of what the compositional differences were or how they affected dispersant action. The interaction of oil and dispersant composition is the most likely source of these differences.

3. Are there changes in oil composition which have relevance to environmental toxicity? Years of discussion have taken place over the question of whether chemically dispersed oil is more or less toxic than mechanically-dispersed oil. Most data show that the bulk toxicity of the two types of dispersions are about equal, although recent studies lean toward the finding that the chemically-dispersed oil is, in fact, less toxic. This finding would indicate that there are compositional changes caused by dispersants.

Dispersant-accelerated weathering (evaporation) has been noted in the past by a number of workers. McAuliffe was the first to publish information on this topic.[1,2,3] This phenomenon was further defined by McAuliffe in subsequent laboratory experiments where it was found that the C_2 to C_{10} hydrocarbons under a chemically-dispersed slick were of a lower concentration than under mechanically-dispersed slicks.[4] McAuliffe subsequently reviewed a number of experiments, both field and laboratory, in which the accelerated weathering of C_2 to C_{10} hydrocarbons was measured.[5] Wilson and co-workers conducted extensive tank experiments and noted a slightly-faster evaporation rate for chemically-treated oil.[6] Anderson and co-workers noted major differences in the toxicity of mechanically and chemically-dispersed oil to shrimp.[7,8] Further studies showed that the lower toxicity of chemically-dispersed oil was due to accelerated evaporation of toxic mono-aromatics.[9] Bowler and co-workers conducted a number of experiments using a laboratory effectiveness apparatus and found that dispersants increased the evaporation rate of oil when comparing treated and untreated oil.[10] Fingas and co-workers found similar accelerated weathering using dispersants on fuel in a model sewer system.[11,12]

No studies dedicated to studying the chemical composition changes after the application of dispersant were found in the literature. Compositional changes in dispersed oil, were however noted by some workers while studying other facets of the dispersion process. Peake and Hodgson noted that water under an oil treated with an undecanoic acid surfactant was enriched in undecane, but attributed the effect to an anomaly which required further study.[13] Wilson and co-workers noted that there was a compositional difference between the starting and dispersed oil, but suggested that the differences may be due to degradation.[5] Shaw and Reidy found compositional changes but correlated these to mixing energy and not presence or absence of a dispersant.[14]

Experimental

Two forms of experiments were performed. First, evaporative loss was measured in laboratory dispersant effectiveness apparatus. Secondly, dispersant tests were performed in the swirling flask apparatus and the starting oil; surface oil, treated but undispersed; and the oil in the water column were analyzed using a gas chromatograph.

In the first set of experiments, three different apparatus were used. The swirling flask apparatus was operated according to published procedure.[15] The MNS (Mackay-Nadeau-Steelman) or Mackay test was operated according to published procedure except that the oil-to-water ratio was maintained at 1:1200.[16] The Warren Springs, Labofina or alternatively, the rolling flask test, was also operated according to published procedure except for the same oil-to-water ratio as above.[17] The same oil-to-water ratio was maintained in all apparatus to eliminate this as a variable and also for the reason that lower ratios have been shown to effect results.[18]

All experiments were run in the same manner; oil was applied to the water surface, the apparatus energized in its regular manner and after the run was completed, the surface oil was removed using 2.5 cm by 2.5 cm sorbent pads (SPC sorbent). These were in turn extracted using 30 mL methylene chloride. Concentrations were determined colorimetrically using a previously-prepared calibration curve. The calibration curves were prepared in analogous fashion to ensure that losses and sorbent efficiencies were accounted for. Results were repeatable to within 10%. The untreated crude oil was processed in the same manner as above to ensure that evaporation was compensated for. To account for accelerated weathering, experiments were done to measure the oil remaining on the surface and that in the water column. The amount lost to accelerated weathering was obtained by subtracting those amounts from the original amount added. The initial or untreated oil quantity was determined to be that amount left after processing in the apparatus without dispersants. This was done to ensure that losses, evaporation and inefficiencies were accounted for. The oil left on top after dispersion was determined using the sorbent procedure described above. Oil in the water column was determined by the published procedure for the apparatus and always involved extracting a portion of the oil and analyzing colorimetrically using a pre-determined standard curve. At least two runs were performed for every apparatus, oil and dispersant combination. If values were outside 15% experiments were repeated until the majority of values were within 15% of each other.

Five oils were used in both experiments. Their properties are given in Table 1. Mousse mix is a name given to a mixture of Bunker C and Alberta Sweet Mixed Blend (ASMB) and is frequently used in our laboratory for physical experiments. The name derives from the high tendency of that mixture to form mousse (water-in-oil emulsion).

Table 1 **Properties of the Oils Used In This Study**

Property	**Condition**	**Oil**				
		ADGO	**ASMB**	**HIBERNIA**	**LAGO MEDIO**	**MOUSSE MIX**
Density	15C	0.953	0.839	0.865	0.872	0.91
Viscosity	cSt at 15C	66	11	55	47	150
Interfacial Tension	mN/m 15C (oil/sea)	6.9	8.4	21	12	
Dispersant Effectiveness	% in Swirl-flask					
	Corexit 9527	61	38	8	7	15
	Enersperse	67	43	10	10	24

Gas chromatographic analysis was used in the second set of experiments to examine the composition of the starting oil, the surface oil and the oil dispersed into the water column. Methylene chloride extracts were performed as described above, effectiveness measured colorimetrically to ensure the consistency of results with those of previous experiments, and then a 0.5 microlitre portion of the extract was injected into a Hewlett-Packard 5890 chromatograph. The chromatographic conditions were as follows: initial temperature - 40^{o}C, initial time - 5.0 minutes, temperature programming rate - 6.0^{o}/min., final temperature - 300^{o}C, final time - 30 min., and attenuation - 2. The column used was a SPB-1 and with helium as the carrier gas at a flow rate of 2.7 mL/min. The hydrogen flow rate for the FID detector was 30 mL/min and the air flow rate 240 mL/min.

A synthetic oil was made and run through the entire experiment to confirm that enrichment of certain n-alkanes as observed in the regular experiment was not a result of breakdown of the dispersant. No compounds other than those in the synthetic oil were evident in the gas chromatograph resulting from this test.

Weathering of Oil

The results of the experiments using laboratory effectiveness apparatus are summarized in Table 2. The values presented in this table are the amounts of oil unaccounted for after the oil on the surface and in the water column were computed, and thus represents the amount lost through evaporation since other losses were compensated for during the calibration procedure.

Table 2 **EVAPORATION IN THREE APPARATUS**

		PERCENTAGE EVAPORATION IN APPARATUS			
OIL	**DISPERSANT**	**SWIRLING FLASK**	**LABOFINA**	**MNS**	**AVERAGE**
ADGO	COREXIT	4	0	0	1
	ENERSPERSE	0	2	3	2
ASMB	COREXIT	25	31	2	19
	ENERSPERSE	11	25	7	14
MOUSSE MIX	COREXIT	15	6	2	8
	ENERSPERSE	9	8	14	10
HIBERNIA	COREXIT	30	18	10	19
	ENERSPERSE	25	4	14	14
LAGO MEDIO	COREXIT	4	3	12	6
	ENERSPERSE	30	12	2	15
					11

The accelerated weathering ranges from 0 to 30 % with an average of 11 %. These values should be taken in context with the error for each of the apparatus used; swirling flask 5%, Labofina 7%, and MNS 10%. All weathering values obtained were positive, thus indicating that despite the measurement error, dispersants always accelerate the weathering of the oil. The accelerated weathering is least in the MNS, as one might expect because the device operates with a high velocity stream of air and this would evaporate the untreated oil to a large extent. If the untreated oil is evaporated to a large extent the loss by accelerated weathering is small, because results are always compared to the weathering of this untreated oil after processing through the entire experiment. These results indicate that an average of 11% of the mass is removed over a short time period by the action of dispersants. Untreated oil would ultimately lose this mass by evaporation over a longer time depending on temperature and wind speed.

The accelerated weathering of oil was also examined in the second round of experiments. The swirling flask apparatus was used and untreated oil, surface oil and oil dispersed into the water column were examined by GC analysis. Examples of the gas chromatography data are displayed in Appendix Figures A1 to A11. The n-alkane peaks were calibrated between C_9 and C_{30} and relative amounts compared using the values from the GC integrator. A computer program was used to analyze the relative amounts of n-alkanes and then draw comparisons between compositions in the three fractions. The results of this analysis are presented in Tables A1 to A4 of the Appendix. Caution should be exercised in using these data, because a number of assumptions were made in the calculation. First, the individual peaks were not calibrated to the quantity of the compound; it was assumed that all the n-alkane compounds yield the same response on the GC detector. This is a relatively safe assumption under normal circumstances, but could yield a small error for large and small n-alkane members. Secondly, comparisons will be made later in this paper to the amount of compounds that are not n-alkanes, whose response is known to be different than the n-alkanes. Again this will produce an error of unknown magnitude, but is impossible to overcome without doing a painstaking calibration of all peaks present. This calibration would not be useful in this case, because the conclusions presented here would still be the same.

All results are summarized in graphical form in Figures 1 to 8. Each graph shows the comparison of the relative content of n-alkanes between two fractions. Each bar represents the arithmetic difference between the percentage content of that n-alkane in the two fractions being compared. A description appears directly on each graph as to which side represents greater concentrations in what fraction. The weathering of oils is shown in the C_9 to C_{13} portion of these graphs. The amount of these compounds present in either the undispersed oil remaining on the top or in the water column is on average less than that in the starting oil. Each of the compounds, up to about C_{13} is about 5% less in abundance than the starting oil. This analysis

Figure 1 Alkane Composition Comparison: Enersperse 700 in the Water

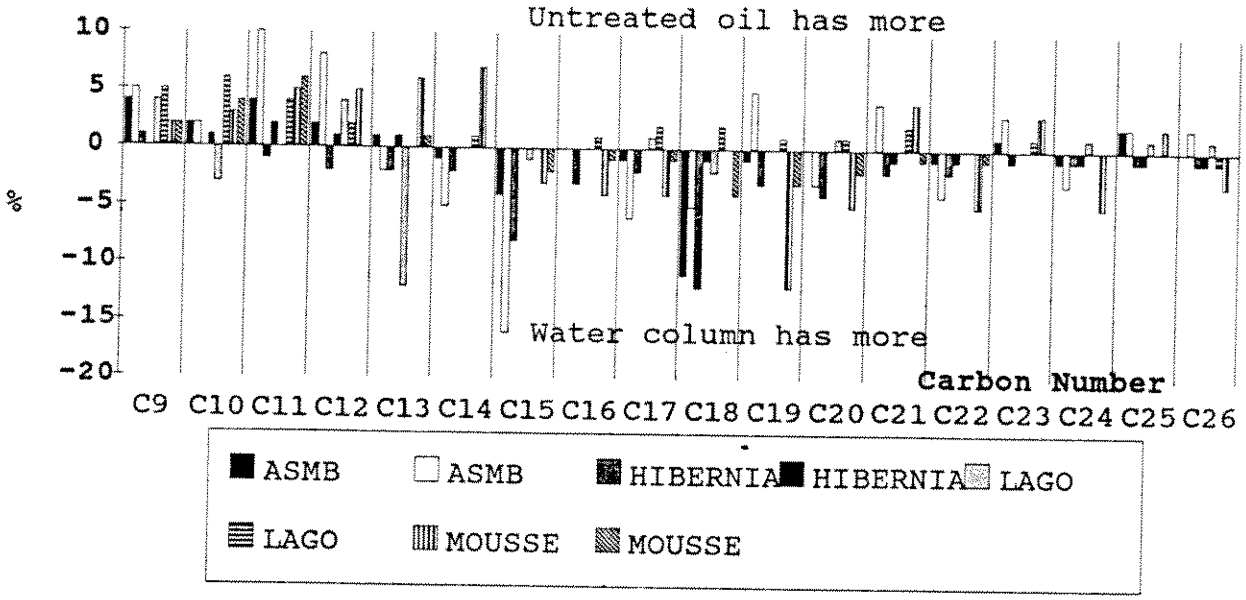


Figure 2 Alkane Composition Comparison: Experimental Dispersant in Water

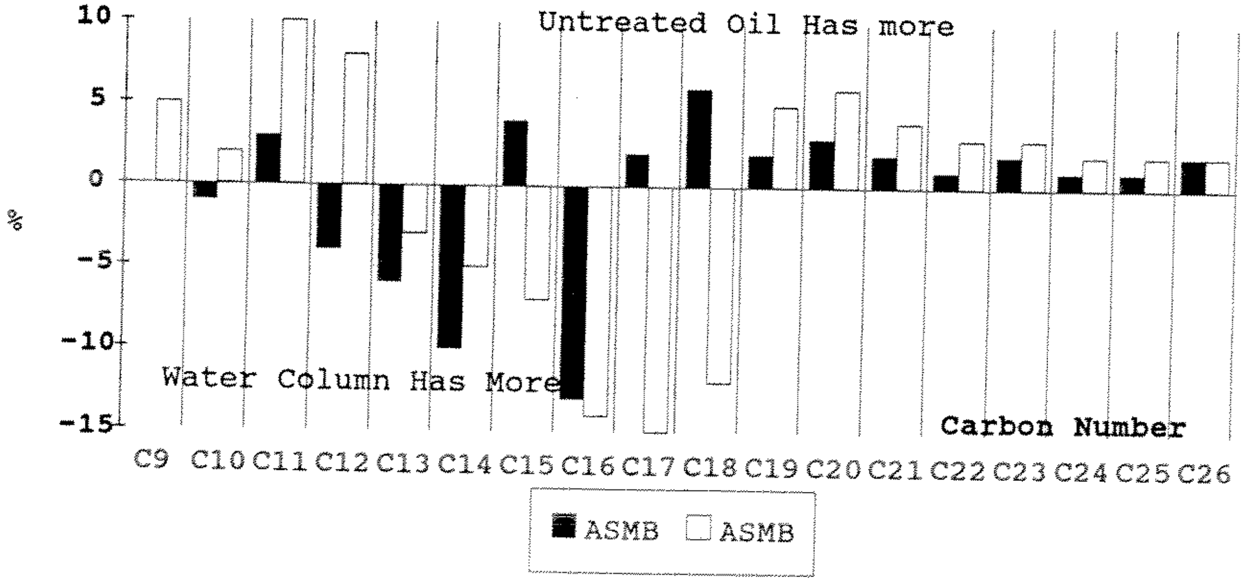


Figure 3 Alkane Composition Comparison: Corexit 9527 in Water

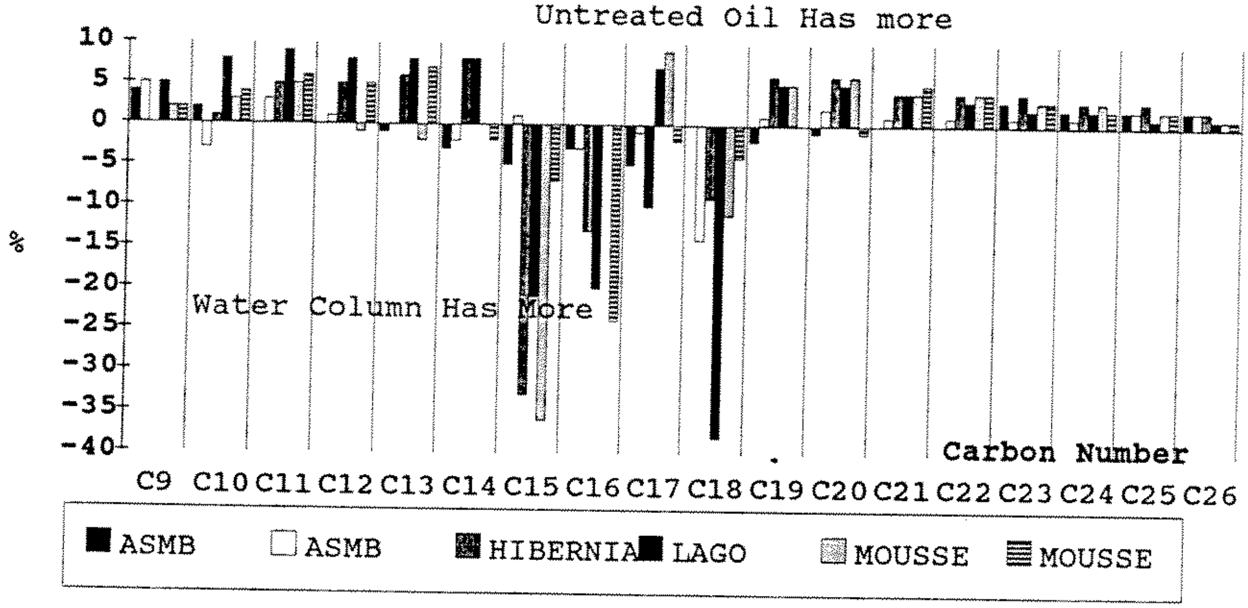


Figure 4 Alkane Composition Comparison: Enersperse 700 and Oil on Top

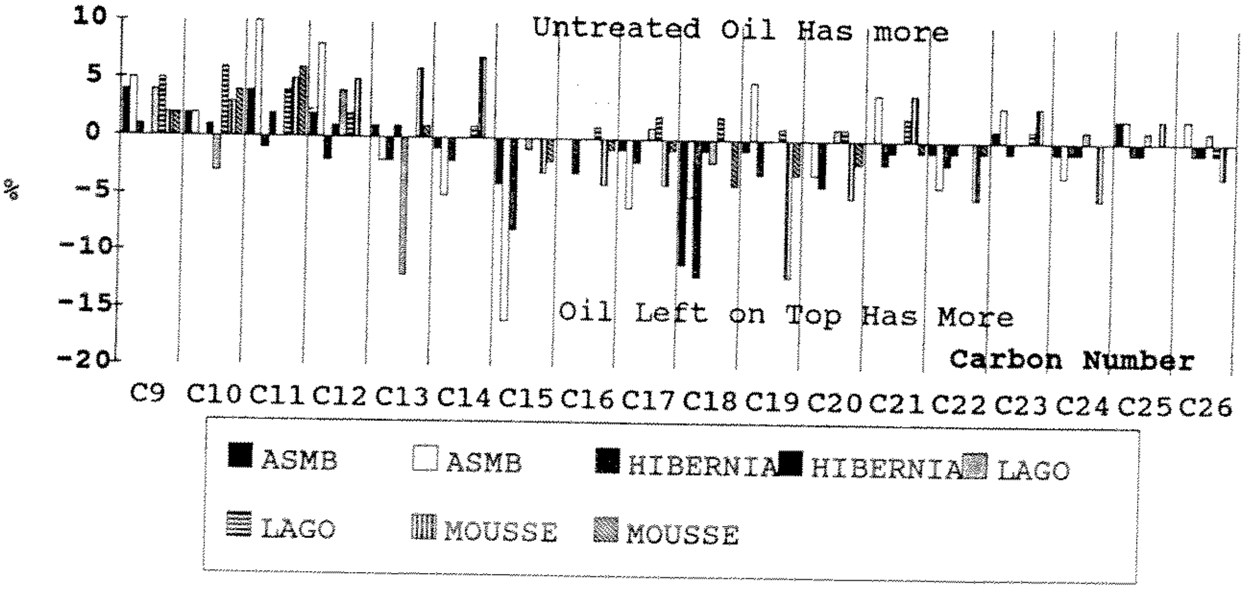


Figure 5 Alkane Composition Comparison: Corexit 9527 and Oil Left on Surface

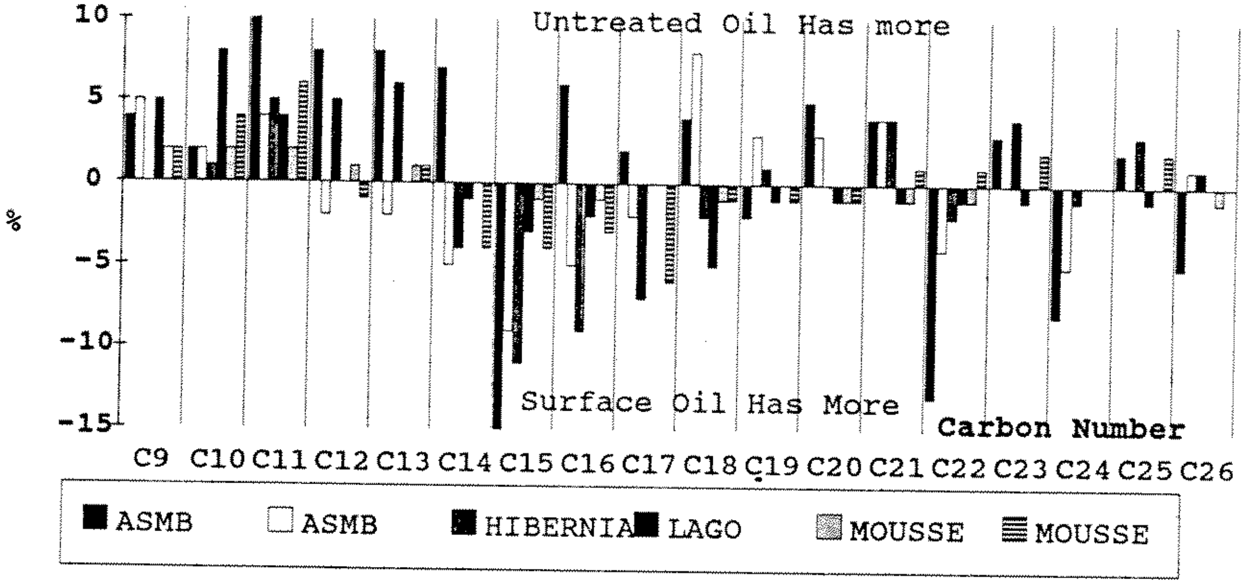


Figure 6 Alkane Composition Comparison: Experimental Dispersant and Oil Left on Surface

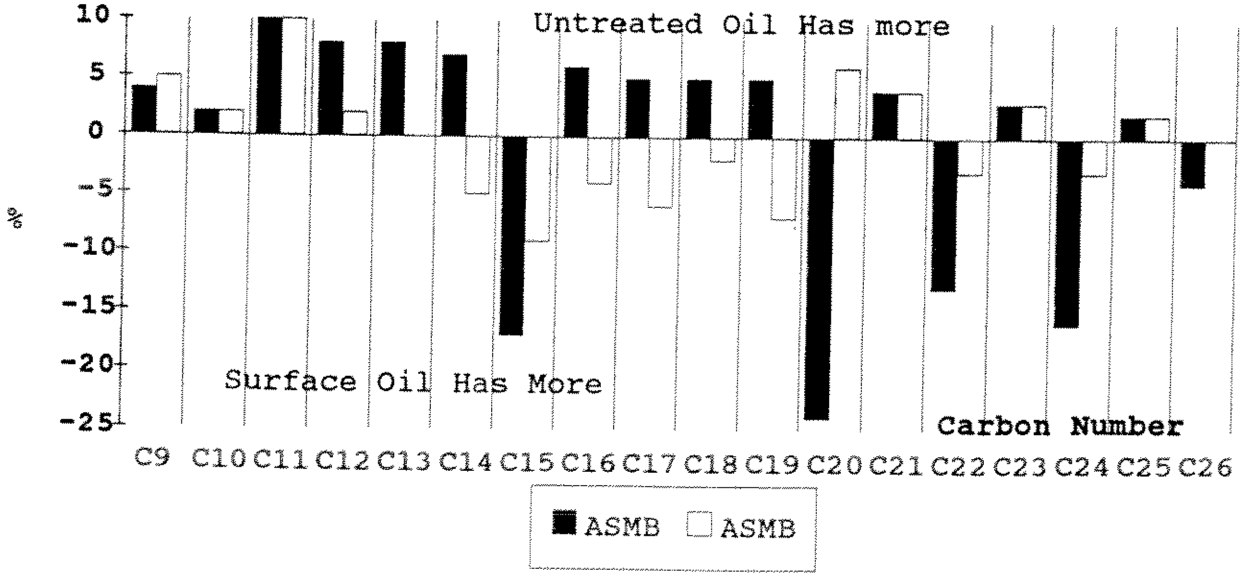


Figure 7 Alkane Composition Comparison: Adgo Crude in water

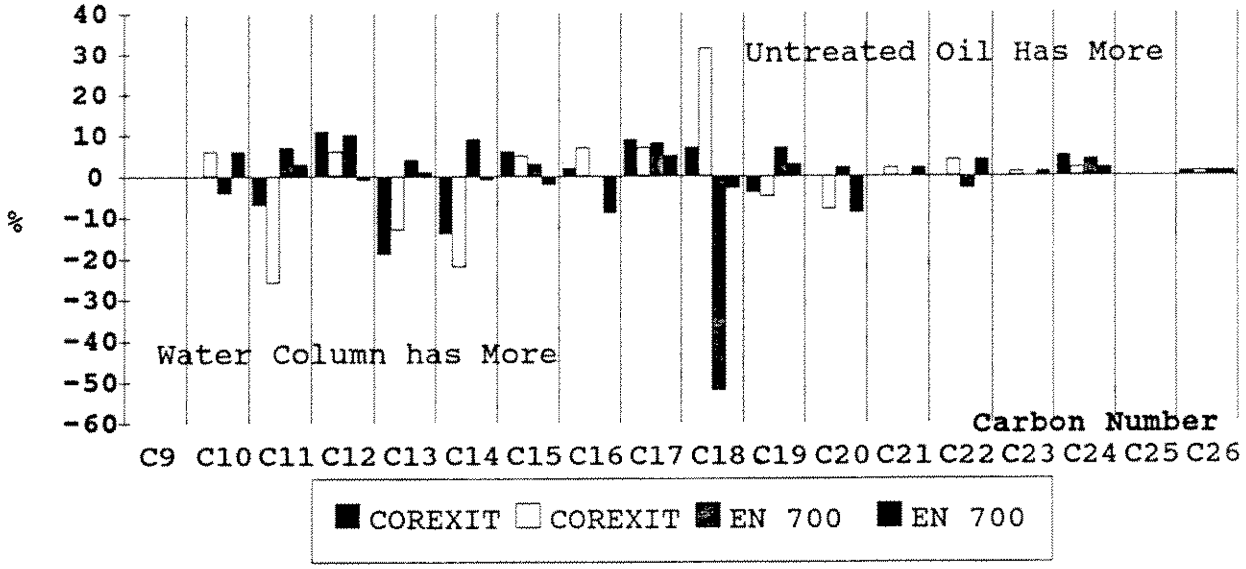
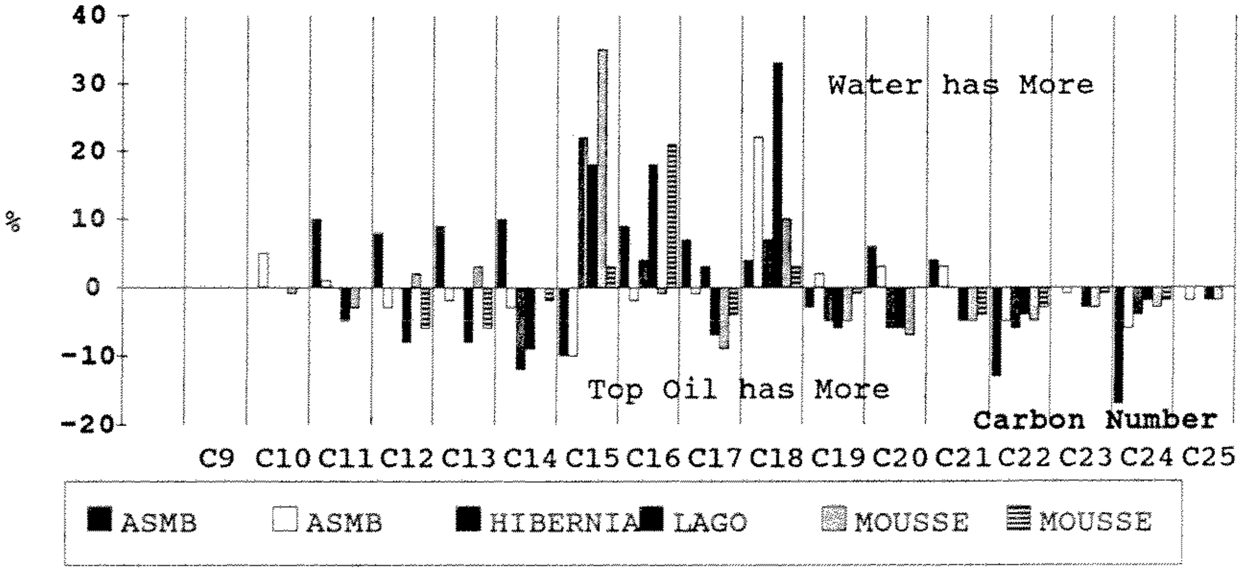


Figure 8 Alkane Composition Comparison: Corexit 9527 in water and on top



shows that accelerated weathering is taking place, even of the n-alkane fractions. The gas chromatographs for the same region of GC analysis show a strong decrease in other compounds present in the water or the undispersed oil remaining on the surface, compared to that of the untreated oil. This indicates that these compounds, largely aromatics, are almost totally removed from the oil during the dispersion process.

Alkane Composition Changes

Three forms of compositional differences have been found:

1. The C_9 to C_{13} n-alkanes in both the undispersed oil remaining on the surface and those in the water column are in lower concentrations than in the starting oil. This is the accelerated weathering as described above.
2. The concentration of certain n-alkanes between C_{13} and C_{18} is much greater in the water column than in the starting oil and is depleted in the surface oil.
3. The concentration of n-alkanes between C_{19} and C_{26} is slightly greater in the undispersed surface oil, than in the untreated oil and the dispersed oil..

These selectivities are illustrated in Figures 1 through 8. Each figure presents a bargraph of the concentration difference at a particular carbon number, between the untreated oil, the oil left on the surface or oil in the water column. Annotation appears on each graph to show which portion of the oil has a greater concentration. The different bars on each graph represent the different crude oils and the key to which oil it is, appears on the bottom of the graph. For most oils two runs were performed and both data sets are presented on the graphs to show the repeatability of these duplicate runs. The exception to this is the separate graph run for Adgo crude, Figure 7, where the different bars represent different dispersants. Adgo has a low n-alkane content and although it shows the same results as other oils, those results are near noise level, which is about 5%.

Figure 1 shows the comparison of n-alkane composition between the untreated oil and the oil in the water column for the dispersant Enersperse 700. This graph shows the three forms of composition change and especially the significant concentration of the C_{13} to C_{18} in the water column compared to the oil used for the experiment. Figure 2 shows a similar effect for an experimental dispersant and Figure 3 shows this effect for Corexit 9527. This latter figure shows the three forms of n-alkane concentration changes very clearly. The difference in dispersants is also illustrated here by comparing the first three figures. Corexit 9527 puts an increased amount of C_{15}, C_{16} and C_{18} into the water column. Enersperse puts an increased amount of C_{13} to C_{19} into the water column. The experimental dispersant does the same except for one carbon number lower than Enersperse. This selection is so unique that one can actually identify which dispersant was used by simple examination of the gas chromatograph.

Figures 4 to 6 show the comparison of the untreated oil with oil left on the top of the water. The alkane selectivity is again evident. The surface oil is depleted in C_9 to C_{12} n-alkanes by accelerated weathering, is somewhat depleted in some of the C_{13} to C_{19} components which are concentrated in the water column and finally the surface oil is enriched in the larger n-alkanes which disperse poorly. Figure 7 shows the same effect with Adgo oil. Figure 8 shows a comparison of oil remaining on the surface versus oil in the water column. Since both fractions have undergone accelerated weathering by dispersant action, the lower alkanes' concentration is not significant. The dispersed oil has more C_{15}, C_{16} and C_{18} as is typical of Corexit 9527. The surface oil shows an increased concentration of larger alkanes well.

These data show that the concentrations of n-alkanes in the dispersed oil and oil left on the surface are altered by the use of surfactants. Two areas of alteration are strongly evident, one falling in carbon numbers 12 to 18 and the other above these values. The former is directly indicative of the type of dispersant used, and in fact could be used to identify the specific dispersant. This selectivity is thought to be a result of absorption of n-alkanes to the oleophilic portion of the surfactant. This occurs at the same chain length as the oleophilic portion or 1 or 2 carbon units shorter. Such phenomena has been observed before and actually is used in designing surfactants for solubilizing materials.[19] It has however never been reported or studied in terms of oil spill dispersants.

The concentrations of the higher alkanes (C_{19} and above) are lower in the dispersed oil than in the starting oil and in the surface oil. This indicates that these components are less dispersable than the shorter alkanes and are concentrated in the undispersed surface layer.

The overall effect of this selectivity is thought to be significant upon the final dispersion effectiveness, but not dominating. Table 3 shows the approximate concentrations of the n-alkanes in the three studied fractions. There appears to be an n-alkane enrichment overall in the water column caused by

Table 3 **Alkane Content**
(Content Determined by GC Analysis of Weathered Fraction only)

		n-Alkane Content (%)			**Alkane Enrichment (%)**	
Oil	**Dispersant**	**Oil**	**Water**	**Top**	**Water**	**Top**
Adgo	Corexit	13	13	25	0	-
	Enersperse	13	37	55	184	-
ASMB	Experimental	43	54	44	26	2
	Corexit	43	68	33	58	-23
	Enersperse	43	66	45	53	5
Hibernia	Corexit	48	44	44	-8	-8
	Enersperse	48	60	47	25	-2
Lago Medio	Corexit	40	87	53	118	32
	Enersperse	40	56	38	40	-5
Mousse Mix	Corexit	44	81	44	84	0
	Enersperse	44	74	54	68	23
				Average	59	1

dispersants. The average alkane enrichment is 59%. The n-alkane fraction content in the surface oil remains about the same. This is consistent with the previous finding, as the depletion of the C_{13} to C_{19} fraction by dispersant action is matched by the increased amount of the larger n-alkanes left on the surface.

The effectiveness of the three dispersants used in this test are in decreasing order; experimental, Enersperse 700 and Corexit 9527. The amount of n-alkanes selected by each of these dispersants decreases in the same order. The experimental dispersant which has a large mixture of chain lengths and therefore concentrates the greater number of different n-alkanes in the water column, is the most effective. There may be a correlation between these facts and that may be a hint for the dispersant designer seeking to improve dispersant effectiveness.

Summary and Conclusions

Dispersants cause accelerated weathering of oil, removing most of the oil components up to C_{12}. The acceleration consists of the removal of about 11% of the oil mass on the short term. Most of the aromatics and some of the n-alkanes are removed.

Dispersants absorb some of the n-alkanes corresponding to their surfactant oleophilic chain lengths, this results in an increased concentration of these compounds in the water column and their depletion in the slick remaining on the surface. This selectivity is unique to the dispersant formulation.

Dispersants do not have as much effect on longer chain n-alkanes ($>C_{19}$) as they do on the shorter ones. The surface oil is enriched in these longer chain n-alkanes.

These three effects, although significant, are not major and do not dominate the dispersion process.

These findings do however, have implications for dispersant design. There appears to be a correlation between the number of different chain lengths in a surfactant (and consequently the n-alkanes concentrated in the water column oil) and the effectiveness. The more surfactant chain lengths present, the greater the effectiveness. Furthermore the finding that the surface oil contains higher concentrations of longer-chain alkanes indicates that this oil is less dispersable than before and also that future dispersant formulation work might concentrate on dispersing more of these compounds into the water.

The fact that dispersants promote accelerated weathering also has implications. First, the application of remote sensing to measure oil dispersion on the sea should include consideration of the additional amount removed by accelerated weathering. Secondly, the removal of the volatile fractions of the oil, many of which are toxic aromatic compounds, implies that over short time periods chemically-dispersed oil would be somewhat less toxic to many organisms than mechanically-dispersed oil at the same concentration.

Acknowledgements

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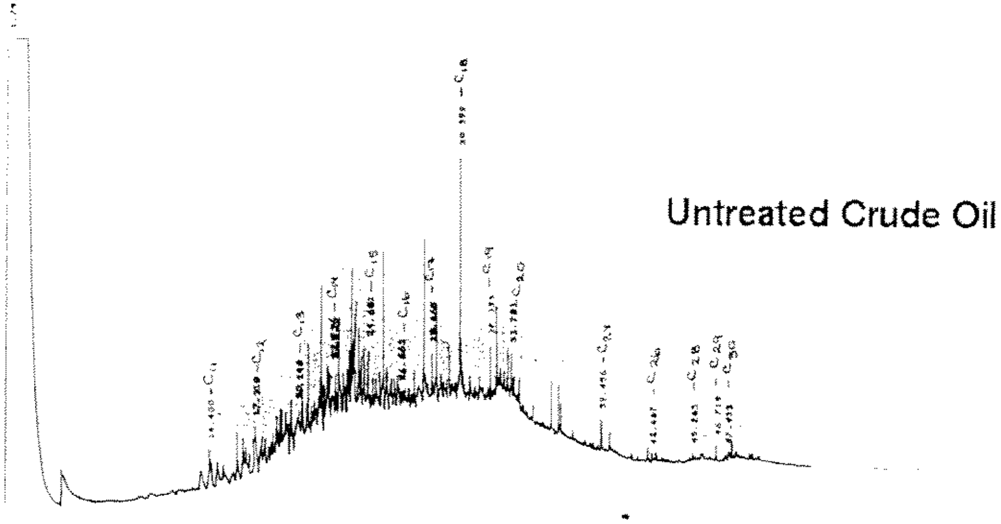
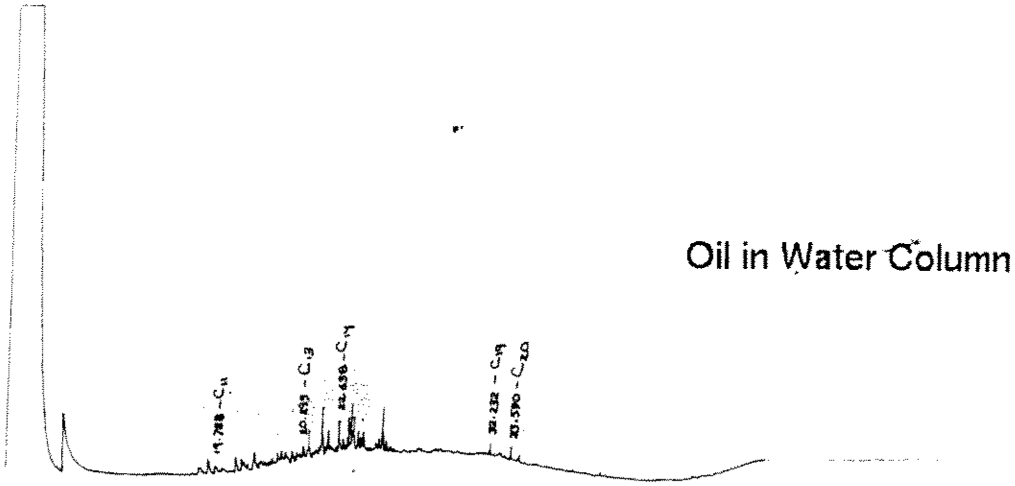
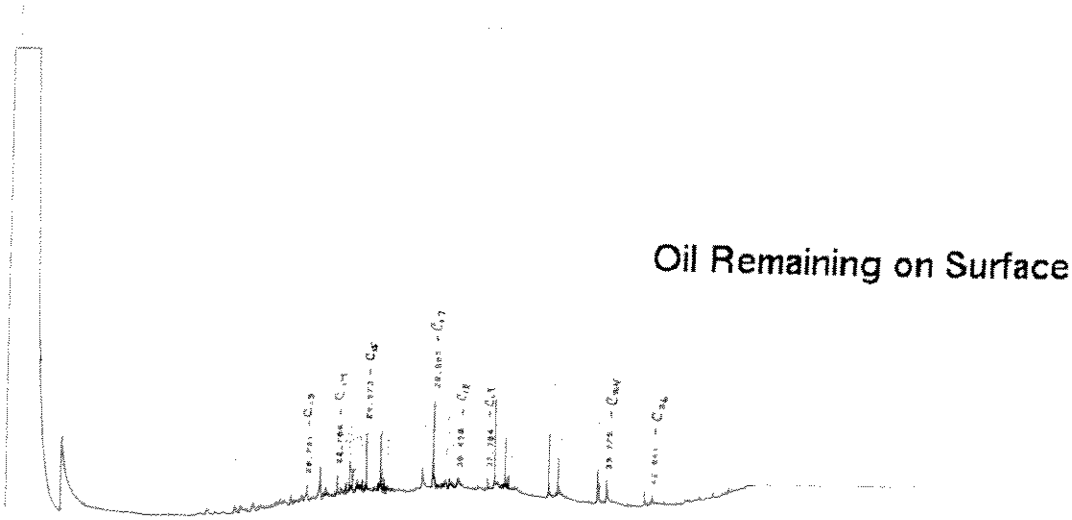
Figure A1 Chromatograms of the Dispersion of Adgo Crude Oil Using Corexit 9527



Untreated Crude Oil

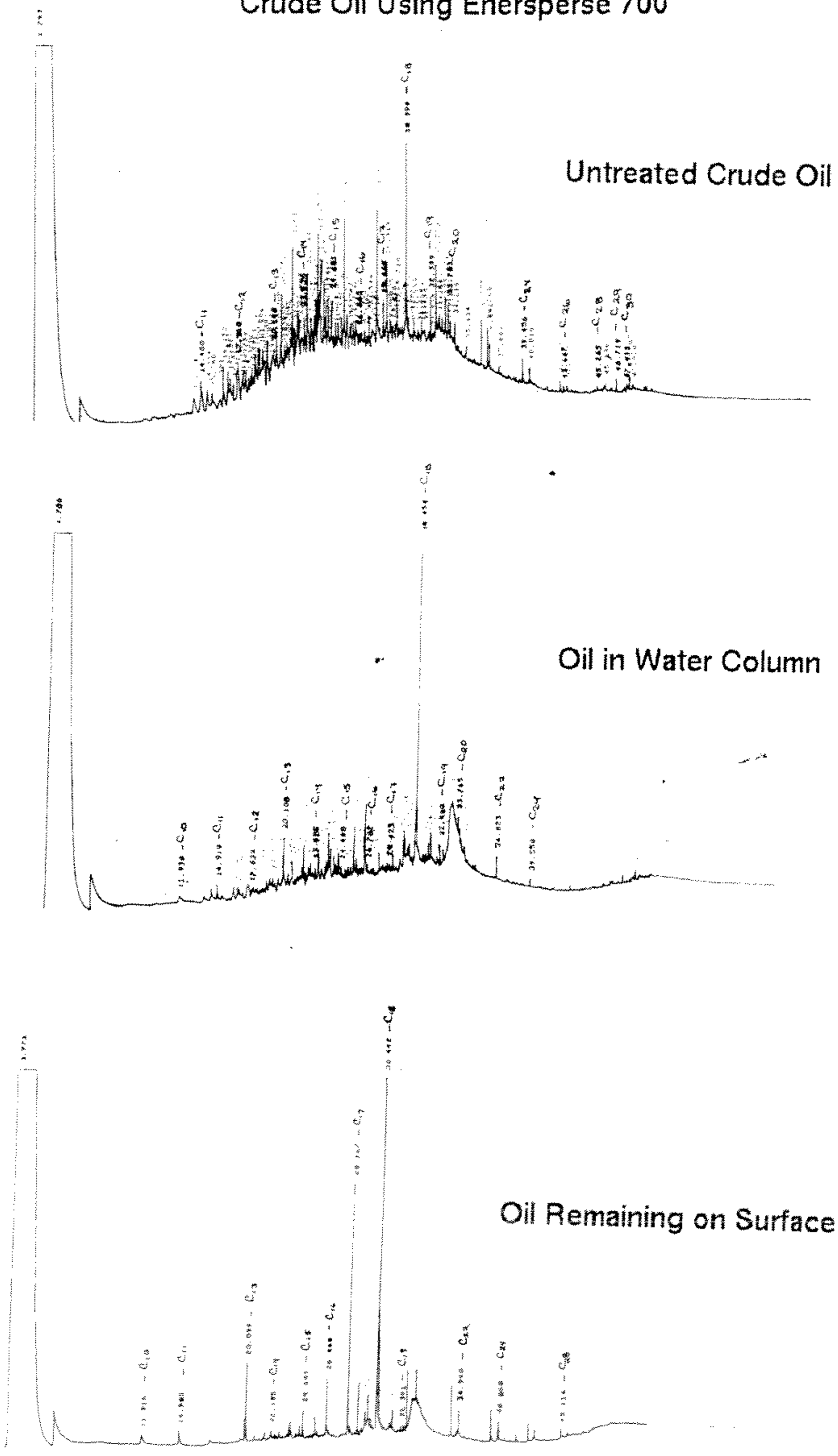


Oil in Water Column



Oil Remaining on Surface

Figure A2 Chromatograms of The Dispersion of Adgo Crude Oil Using Enersperse 700

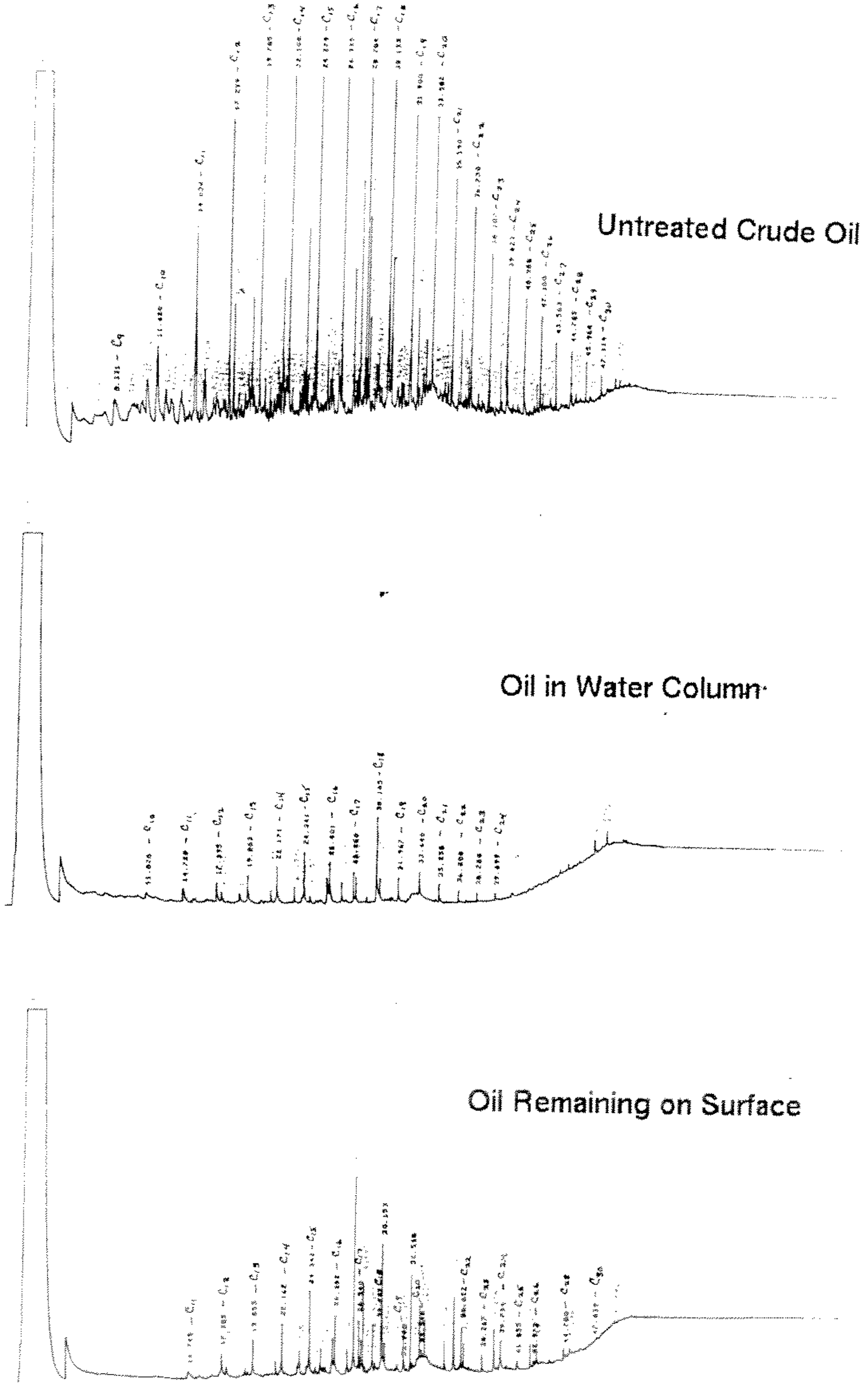


Untreated Crude Oil

Oil in Water Column

Oil Remaining on Surface

Figure A4 Chromatograms of the Dispersion of ASMB Crude Oil Using Corexit 9527

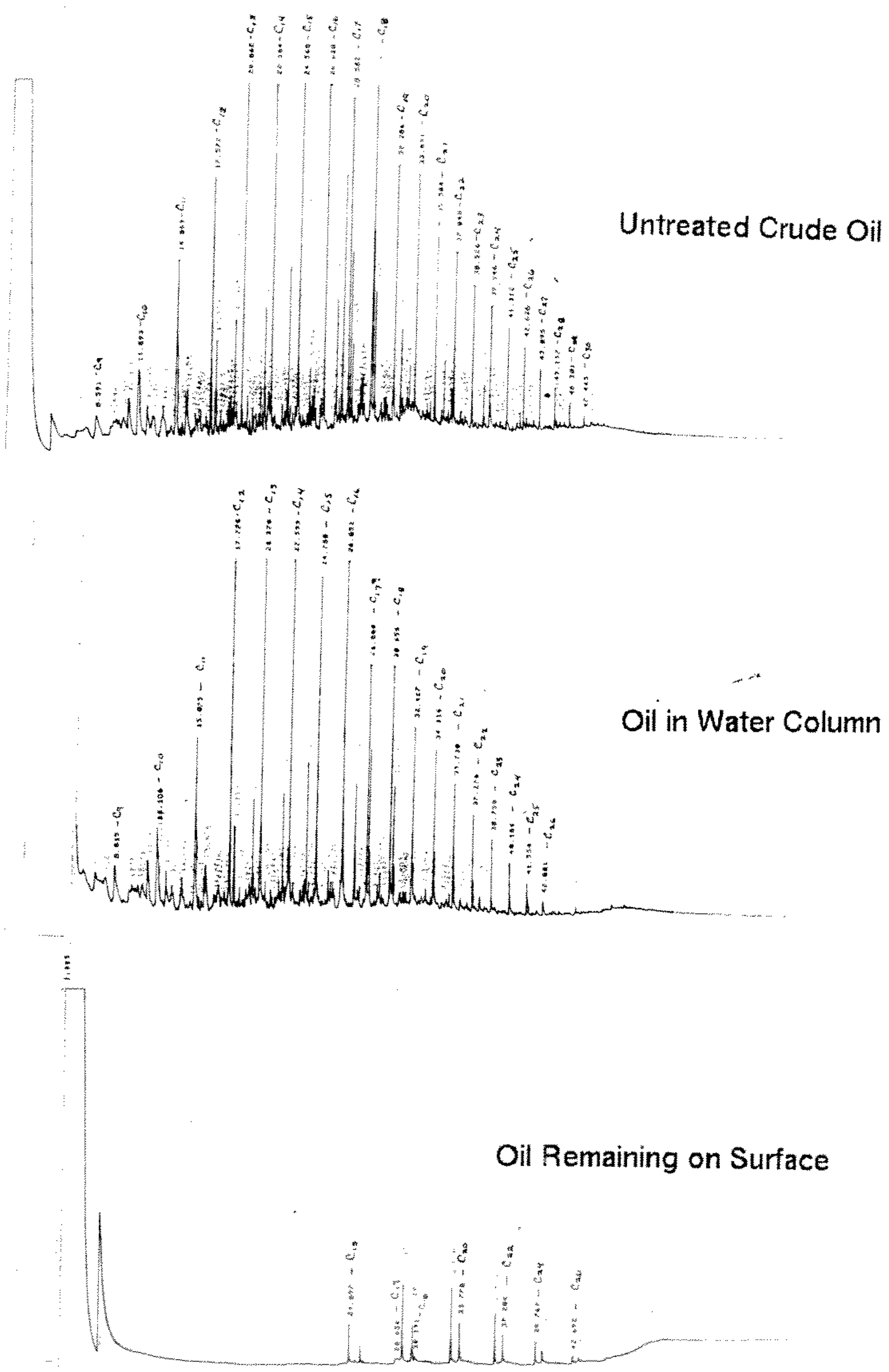


Untreated Crude Oil

Oil in Water Column

Oil Remaining on Surface

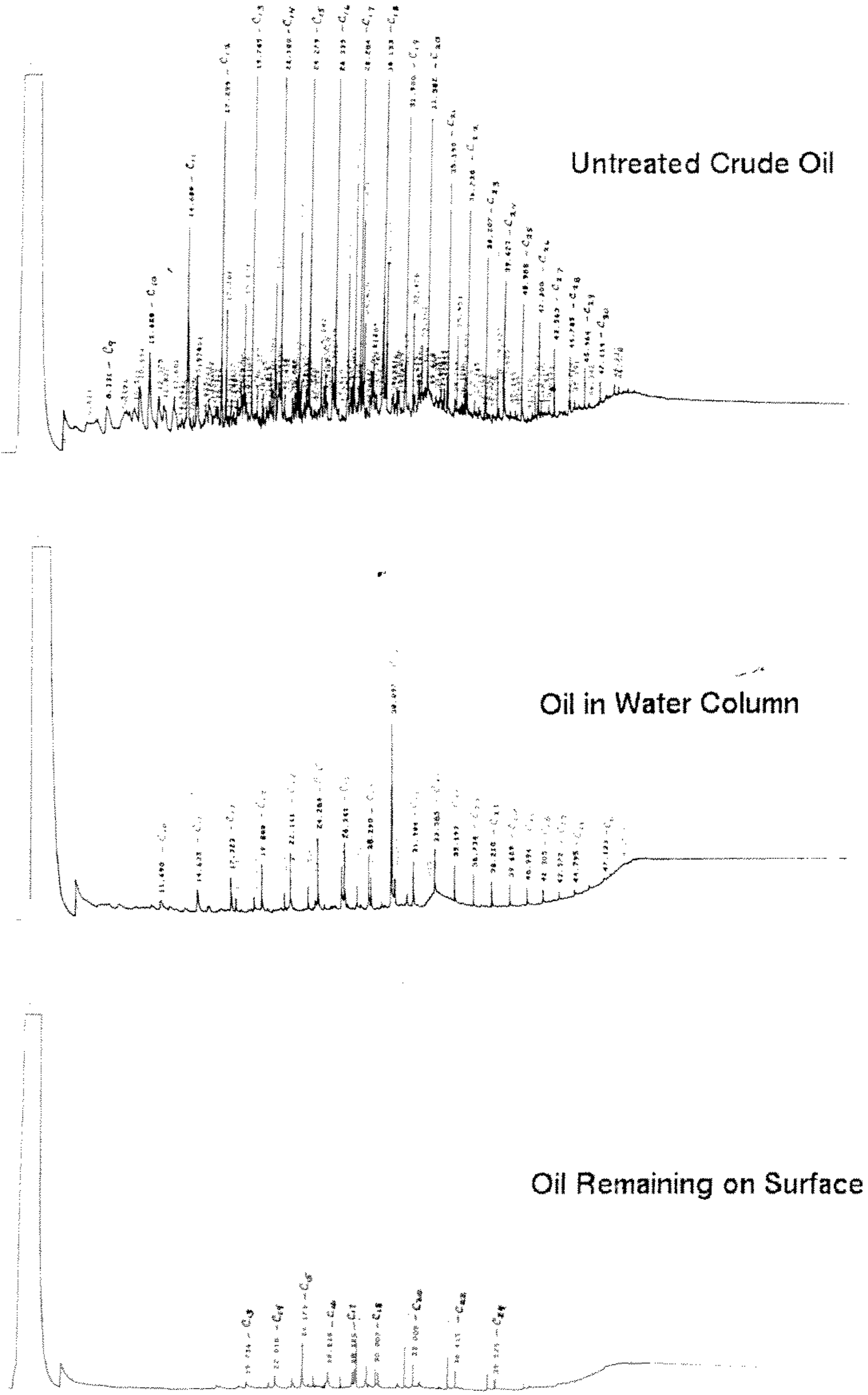
Figure A3 Chromatograms of the Dispersion of ASMB Crude Oil Using Experimental BQ


Untreated Crude Oil

Oil in Water Column

Oil Remaining on Surface

Figure A5 Chromatograms of the Dispersion of ASMB Crude Oil Using Enersperse 700


Untreated Crude Oil

Oil in Water Column

Oil Remaining on Surface

Figure A6 Chromatograms of the Dispersion of Hibernia Crude Oil Using Corexit 9527

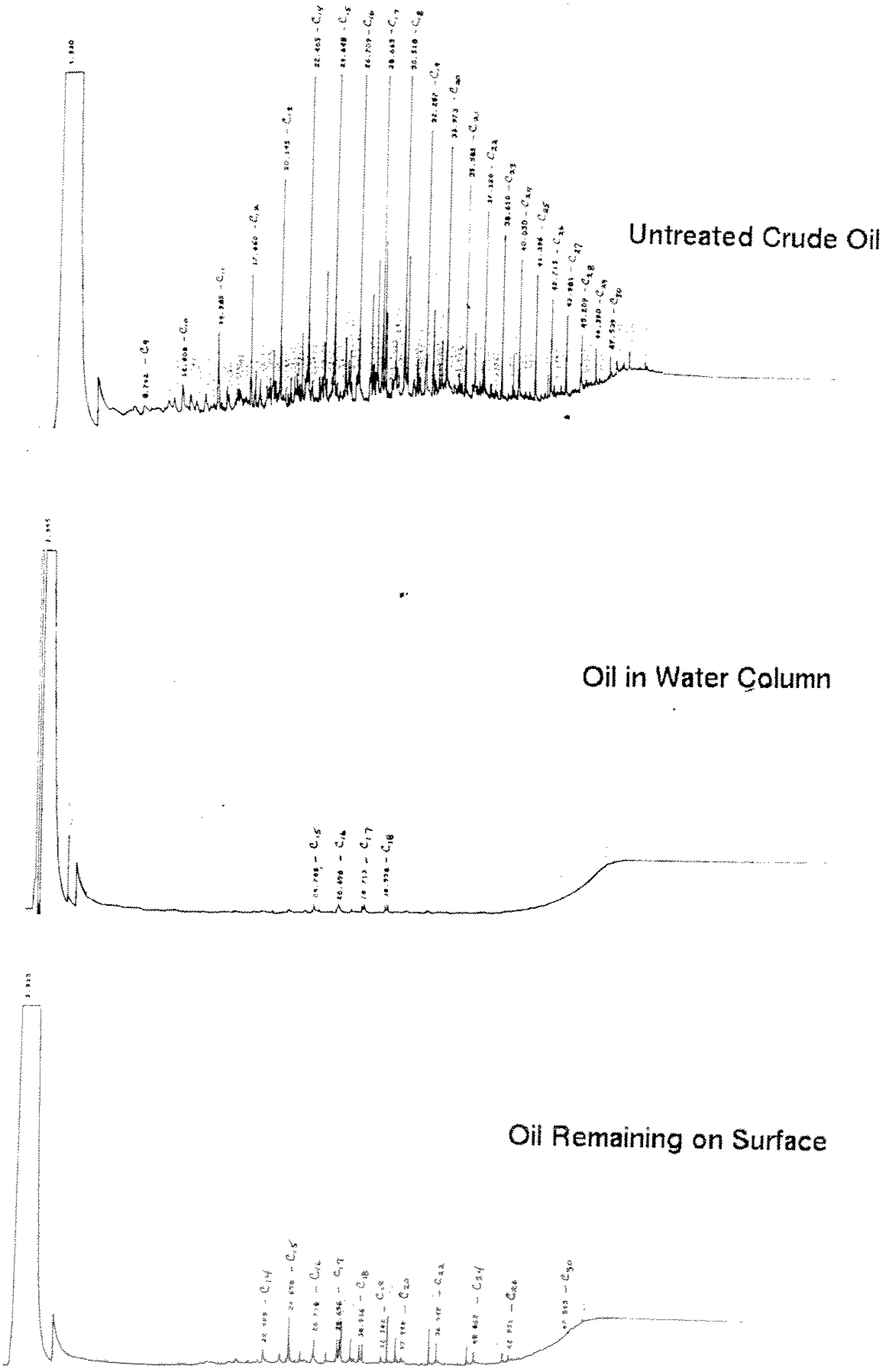
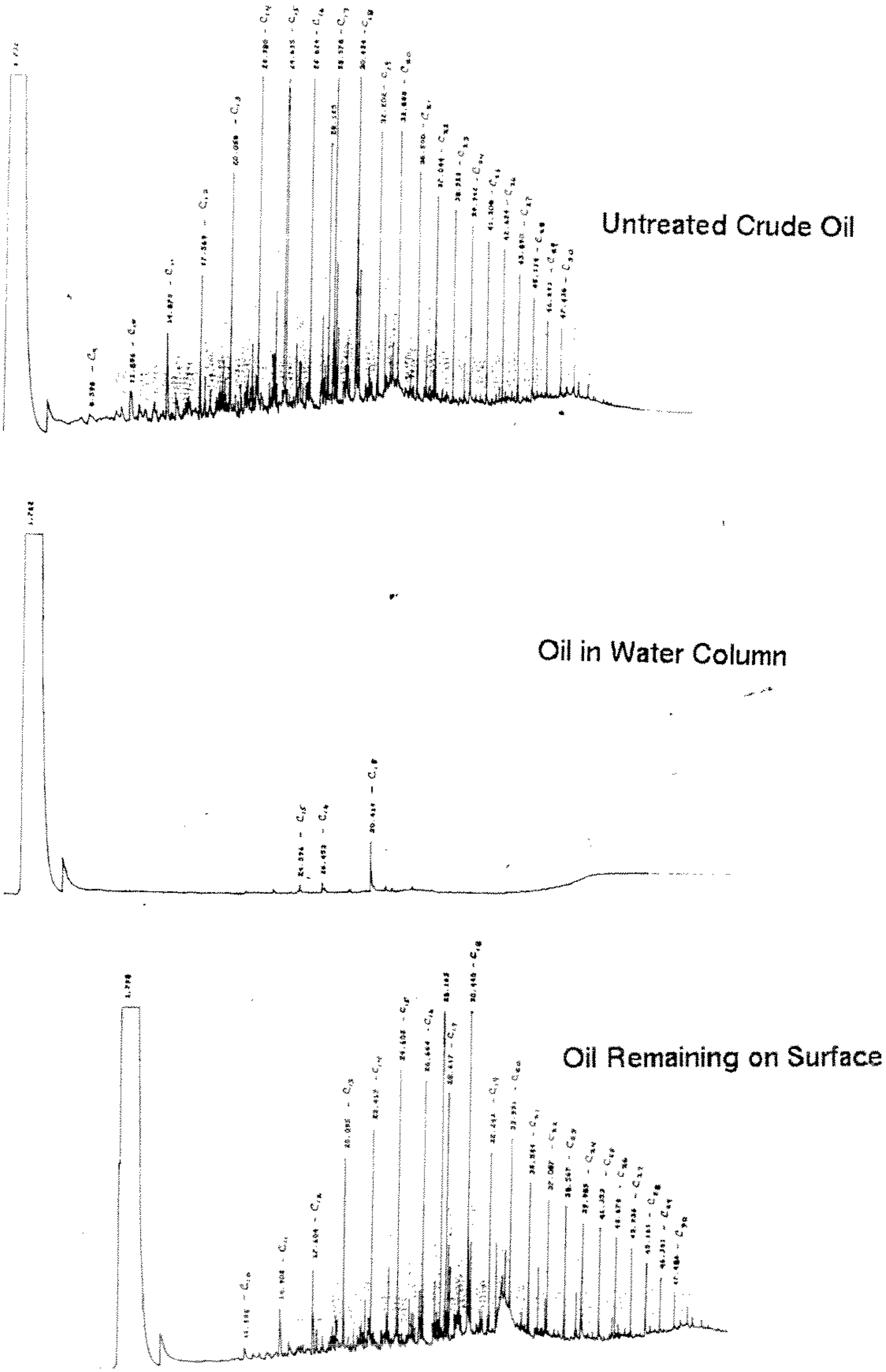


Figure A7 Chromatograms of the Dispersion of Hibernia Crude Oil Using Enersperse 700

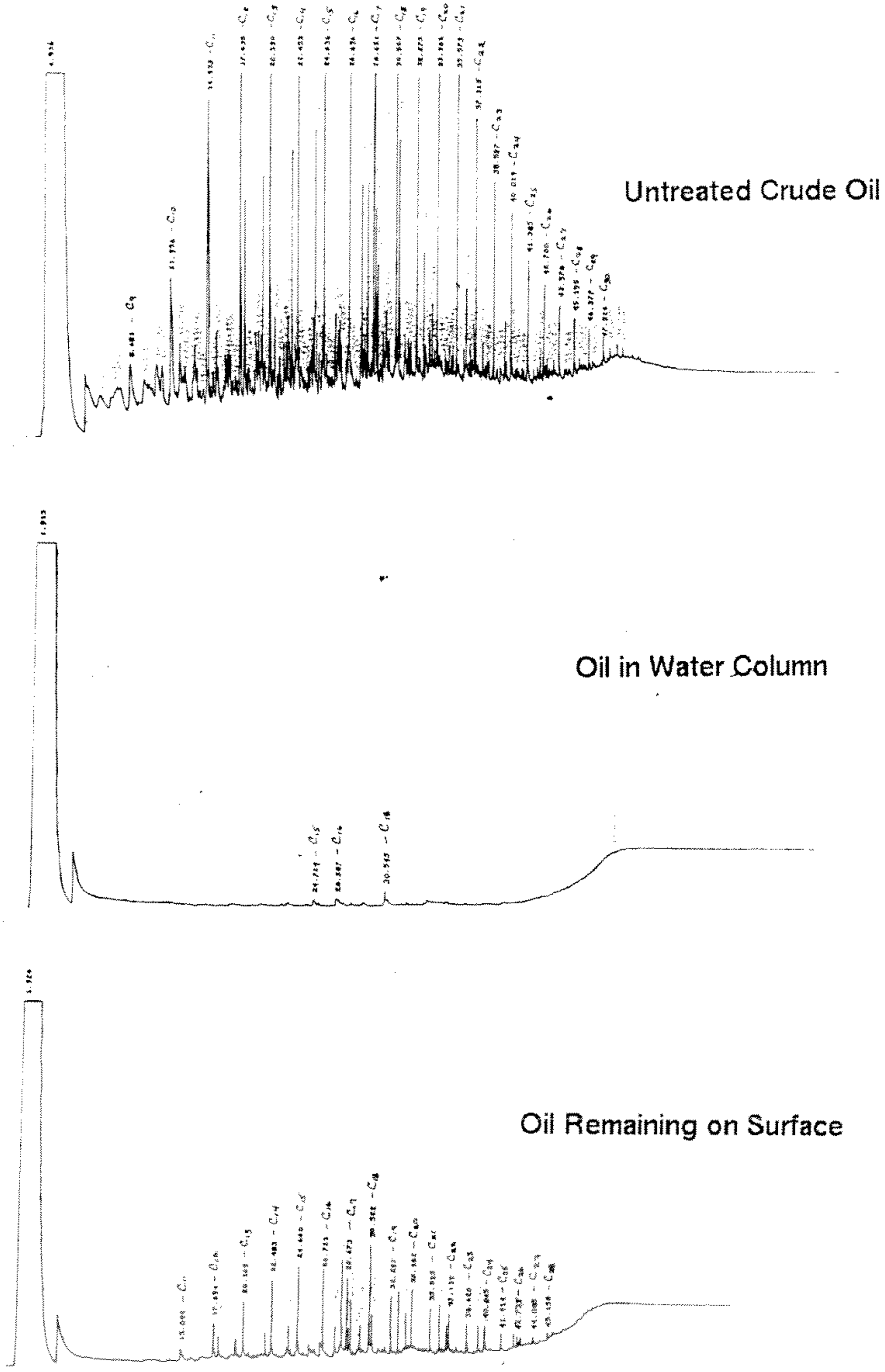


Untreated Crude Oil

Oil in Water Column

Oil Remaining on Surface

Figure A8 Chromatograms of the Dispersion of Lago Medio Crude Oil Using Corexit 9527


Untreated Crude Oil

Oil in Water Column

Oil Remaining on Surface

Figure A9 Chromatograms of the Dispersion of Lago Medio Crude Oil Using Enersperse 700

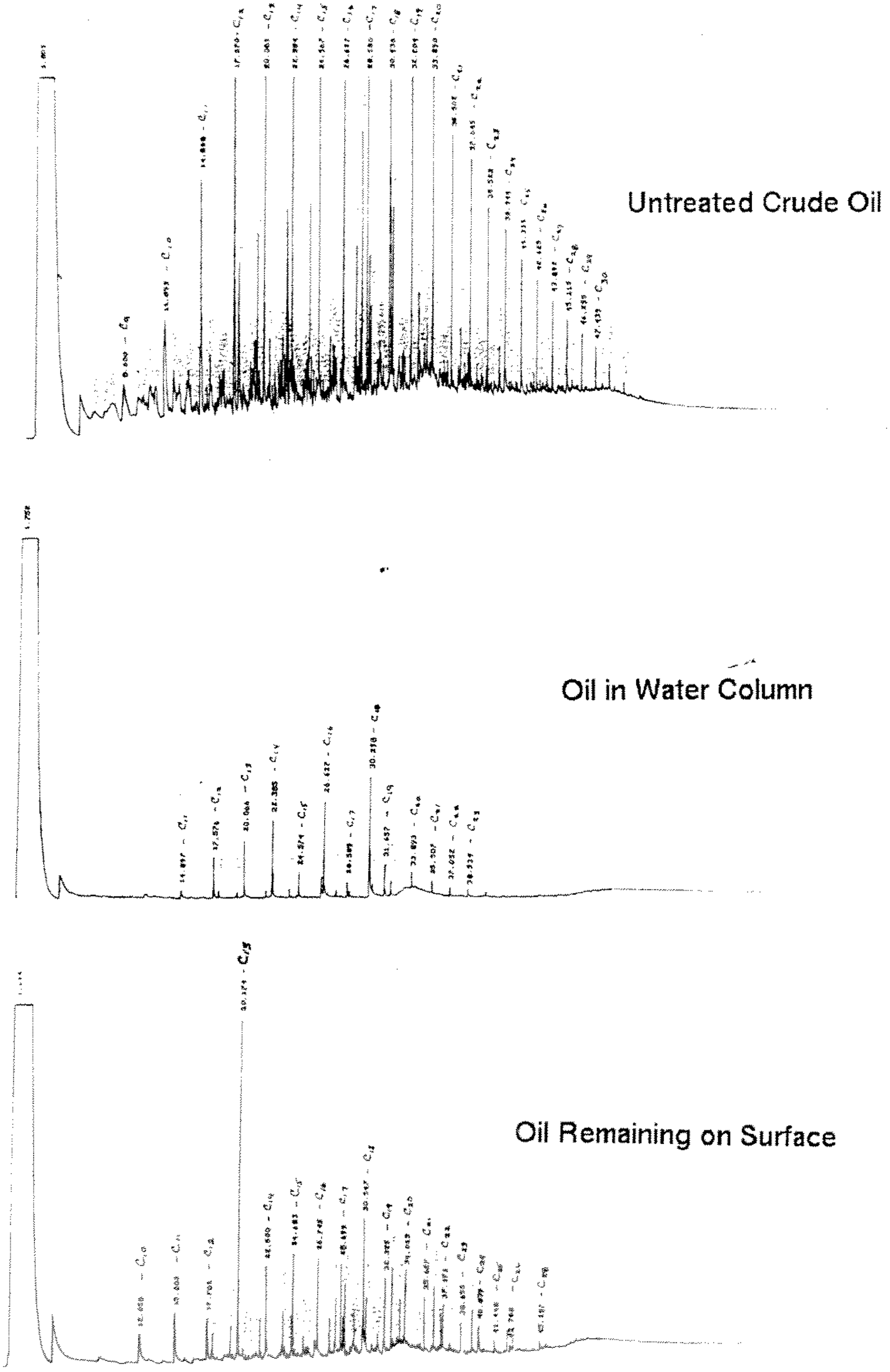
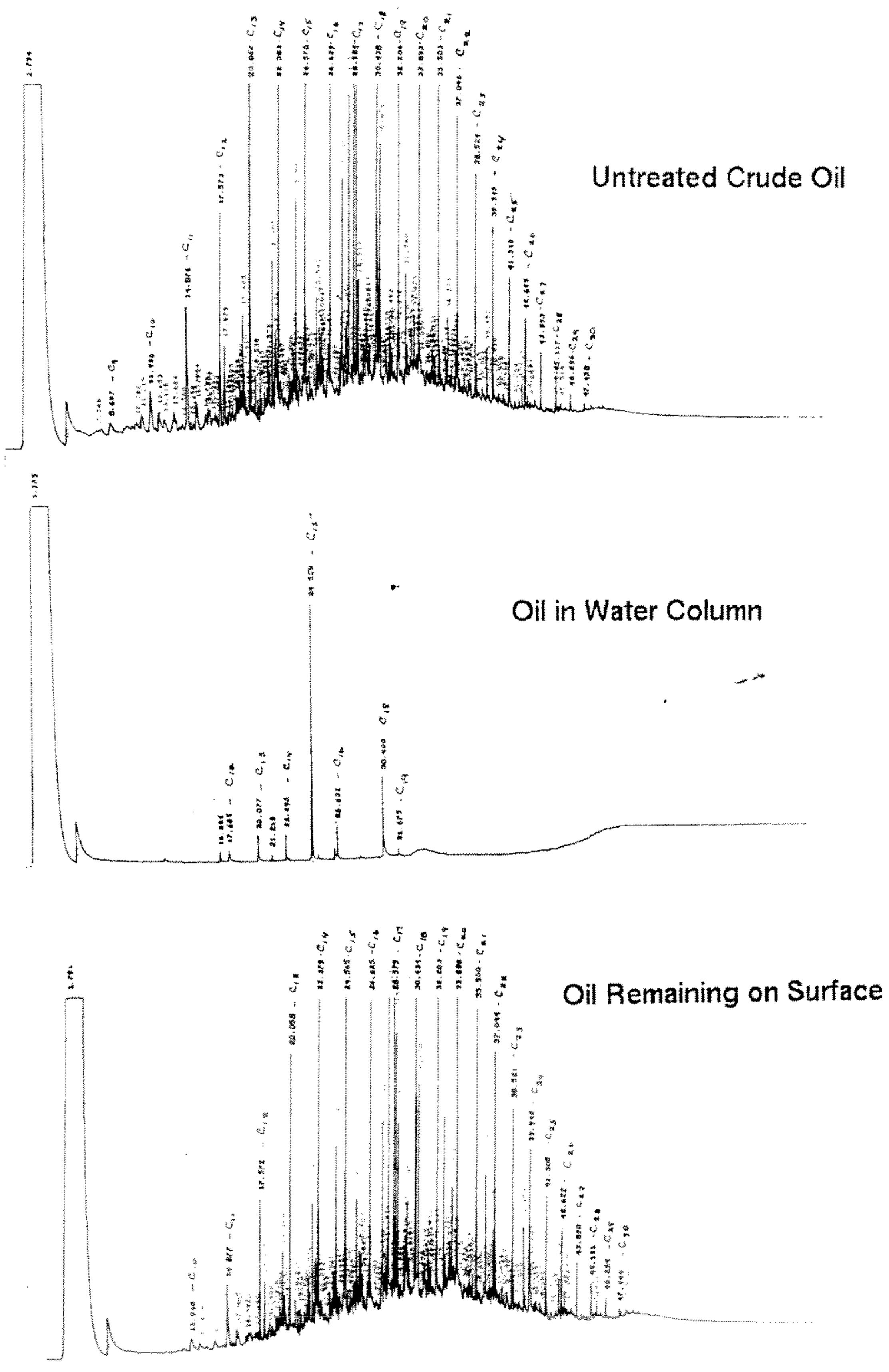


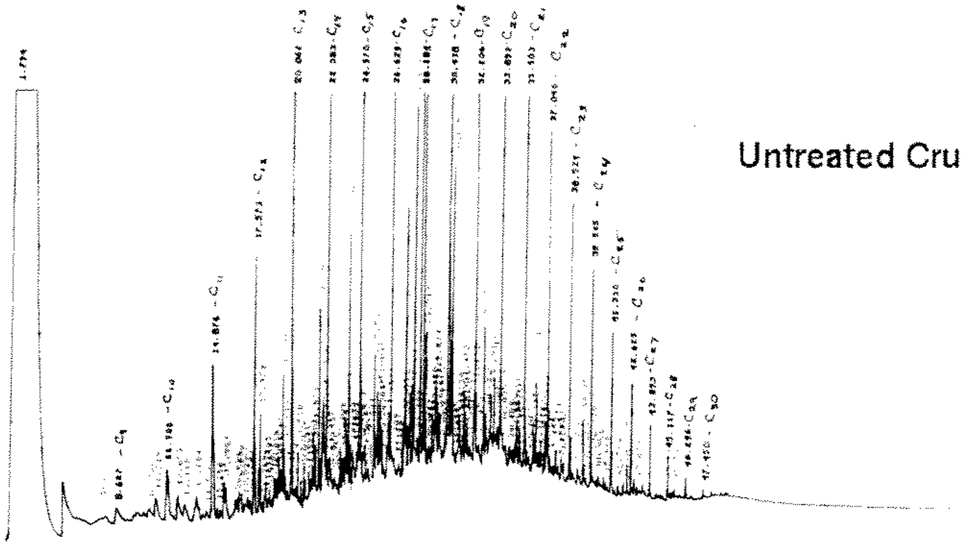
Figure A10 Chromatograms of the Dispersion of Mousse Mix Crude Oil Using Corexit 9527

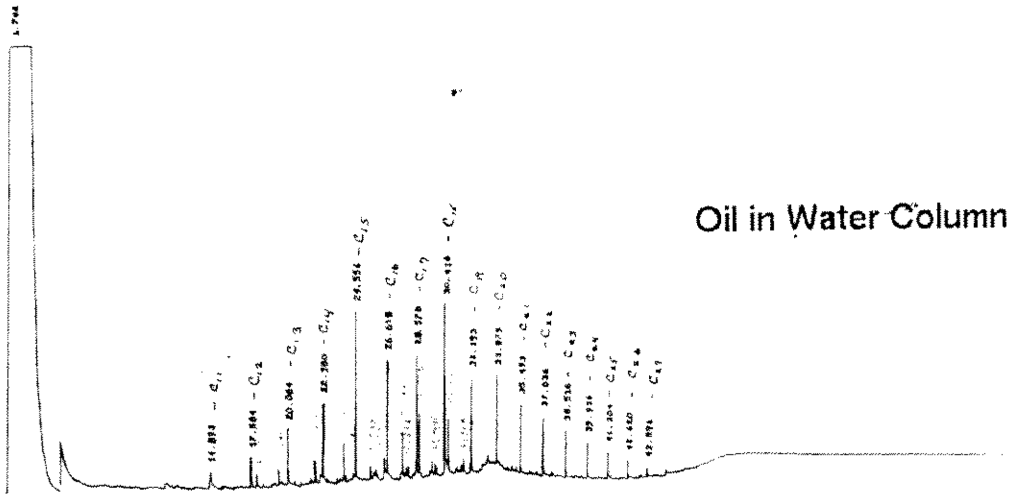

Untreated Crude Oil

Oil in Water Column

Oil Remaining on Surface

Figure A11 Chromatograms of the Dispersion Of Mousse Mix Crude Oil Using Enersperse 700


Untreated Crude Oil


Oil in Water Column

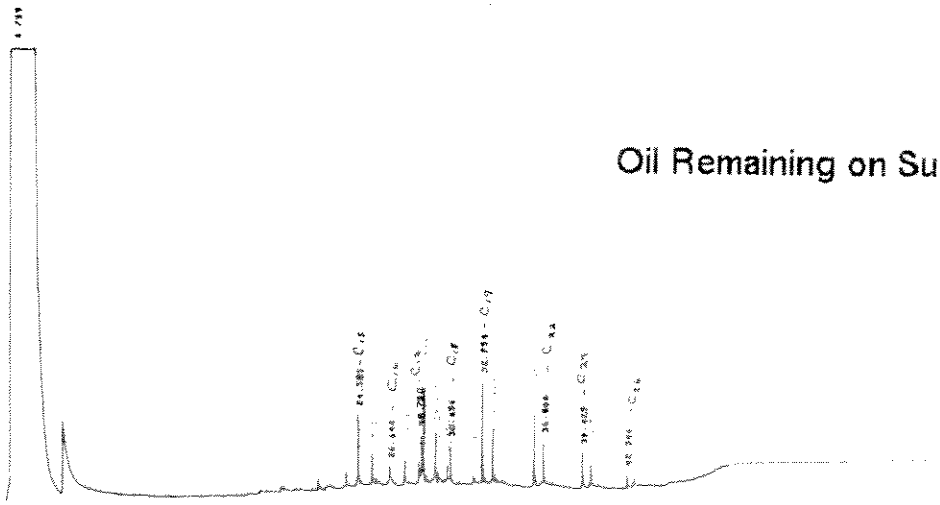

Oil Remaining on Surface

Table A1 **CHANGES IN WATER ALKANE COMPOSITION AFTER DISPERSION**

COREXIT 9527 **PERCENTAGE CHANGE BY CARBON NUMBER**

OIL	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
ASMB	4	2	0	0	-1	-3	-5	-3	-5	0	-2	-1	0	0	3	2	2	2
ASMB	5	-3	3	1	0	-2	1	-3	-1	-14	1	2	1	1	1	1	2	2
HIBERNIA	0	1	5	5	6	8	-33	-13	-10	-9	6	6	4	4	4	3	3	2
LAGO	5	8	9	8	8	8	-21	-20	7	-38	5	5	4	3	2	2	1	1
MOUSSE	2	3	5	-1	-2	0	-36	0	9	-11	5	6	4	4	3	3	2	1
MOUSSE	2	4	6	5	7	-2	-7	-24	-2	-4	0	-1	5	4	3	2	2	1

EN 700 **PERCENTAGE CHANGE BY CARBON NUMBER**

OIL	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
ASMB	4	-2	6	-7	5	4	-8	1	-5	-10	-3	0	2	0	2	2	2	2
ASMB	5	-3	3	3	3	0	2	0	1	-16	1	0	1	0	1	0	0	1
HIBERNIA	1	2	3	2	3	4	3	-13	4	-63	3	3	2	2	2	2	2	2
HIBERNIA	0	1	5	5	6	8	11	-29	8	-55	6	6	4	4	4	3	3	2
LAGO	4	7	5	-3	-4	-6	4	-10	3	-16	-1	3	1	1	0	2	2	2
LAGO	5	8	9	8	8	8	-91	6	7	7	5	5	4	3	2	2	1	1
MOUSSE	2	3	1	1	1	0	1	0	-1	-5	0	-1	-1	0	0	0	0	0
MOUSSE	2	4	6	5	2	-1	-1	-2	-3	-11	-2	-2	-1	-1	0	2	2	1

EXPT'L BQ **PERCENTAGE CHANGE BY CARBON NUMBER**

OIL	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
ASMB	0	-1	3	-4	-6	-10	4	-13	2	6	2	3	2	1	2	1	1	2
ASMB	5	2	10	8	-3	-5	-7	-14	-15	-12	5	6	4	3	3	2	2	2

Table A2 **CHANGES IN SURFACE ALKANE COMPOSITION AFTER DISPERSION**

COREXIT 9527 **PERCENTAGE CHANGE BY CARBON NUMBER**

OIL	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
ASMB	4	2	10	8	8	7	-15	6	2	4	-2	5	4	-13	3	-8	2	-5
ASMB	5	2	4	-2	-2	-5	-9	-5	-2	8	3	3	4	-4	0	-5	0	1
HIBERNIA	0	1	5	5	6	-4	-11	-9	-7	-2	1	0	4	-2	4	-1	3	1
LAGO	5	8	4	0	0	-1	-3	-2	0	-5	-1	-1	-1	-1	-1	0	-1	0
MOUSSE	2	2	2	1	1	0	-1	-1	0	-1	0	-1	-1	-1	0	0	0	-1
MOUSSE	2	4	6	-1	1	-4	-4	-3	-6	-1	-1	-1	1	1	2	0	2	0

EN 700 **PERCENTAGE CHANGE BY CARBON NUMBER**

OIL	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
ASMB	4	2	4	2	1	-1	-4	0	-1	-11	-1	0	0	-1	1	-1	2	0
ASMB	5	2	10	8	-2	-5	-16	0	-6	-5	5	-3	4	-4	3	-3	2	2
HIBERNIA	1	0	-1	-2	-2	-2	-8	-3	-2	-12	-3	-4	-2	-2	-1	-1	-1	-1
HIBERNIA	0	1	2	1	1	0	0	0	0	-1	0	0	-1	-1	0	-1	-1	-1
LAGO	4	-3	0	4	-12	0	-1	0	1	-2	0	1	0	0	0	1	1	1
LAGO	5	6	4	2	0	1	0	1	2	2	1	1	2	0	1	0	0	-1
MOUSSE	2	3	5	5	6	7	-3	-4	-4	0	-12	-5	4	-5	3	-5	2	-3
MOUSSE	2	4	6	0	1	0	-2	-1	-1	-4	-3	-2	-1	-1	0	0	0	0

EXPT'L BQ **PERCENTAGE CHANGE BY CARBON NUMBER**

OIL	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
ASMB	4	2	10	8	8	7	-17	6	5	5	5	-24	4	-13	3	-16	2	-4
ASMB	5	2	10	2	0	-5	-9	-4	-6	-2	-7	6	4	-3	3	-3	2	0

Table A3 **CHANGES IN ALKANE COMPOSITION AFTER DISPERSION**

ADGO

PERCENTAGE CHANGE BY CARBON NUMBER (WATER)

DISPERSANT	**C9**	**C10**	**C11**	**C12**	**C13**	**C14**	**C15**	**C16**	**C17**	**C18**	**C19**	**C20**	**C21**	**C22**	**C23**	**C24**	**C25**	**C26**
COREXIT 9527	0	0	-7	11	-19	-14	6	2	9	7	-4	0	0	0	0	5	0	1
COREXIT 9527	0	6	-26	6	-13	-22	5	7	7	31	-5	-8	2	4	1	2	0	1
EN 700	0	-4	7	10	4	9	3	0	8	-52	7	2	0	-3	0	4	0	1
EN 700	0	6	3	-1	1	-1	-2	-9	5	-3	3	-9	2	4	1	2	0	1

PERCENTAGE CHANGE IN CARBON NUMBER (SURFACE)

DISPERSANT	**C9**	**C10**	**C11**	**C12**	**C13**	**C14**	**C15**	**C16**	**C17**	**C18**	**C19**	**C20**	**C21**	**C22**	**C23**	**C24**	**C25**	**C26**
COREXIT 9527	0	6	8	6	4	-1	-6	7	-20	31	-24	5	2	4	1	-11	0	-5
COREXIT 9527	0	0	12	11	-6	2	-16	2	-19	-1	6	12	0	0	0	-4	0	-3
EN 700	0	-4	9	11	2	10	2	-5	-13	-34	9	12	0	-3	0	3	-1	-1
EN 700	0	6	8	6	4	1	-3	-8	-11	1	3	-4	2	-1	1	-3	0	-2

Table A4 **DIFFERENCE IN ALKANE COMPOSITION BETWEEN THE WATER AND THE SURFACE OIL** (+VE WATER HAS MORE)

EXPT'L BQ	PERCENTAGE CHANGE BY CARBON NUMBER																	
OIL	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
ASMB	0	0	0	-6	3	0	-2	10	9	10	-12	0	0	-6	0	-5	0	-2
ASMB	4	3	7	12	14	17	-21	19	3	-1	3	-27	2	-14	1	-17	1	-6

EN 700	PERCENTAGE CHANGE BY CARBON NUMBER																	
OIL	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
ASMB	0	4	-2	9	-4	-5	4	-1	4	-1	2	0	-2	-1	-1	-3	0	-2
ASMB	0	5	7	5	-5	-5	-18	0	-7	11	4	-3	3	-4	2	-3	2	1
HIBERNIA	0	-2	-4	-4	-5	-6	7	10	-6	51	-6	-7	-4	-4	-3	-3	-3	-3
HIBERNIA	0	0	-3	-4	-5	-8	-11	29	-8	54	-6	-6	-5	-5	-4	-4	-4	-3
LAGO	0	-10	-5	7	-8	6	-5	10	-2	14	1	-2	-1	-1	0	-1	-1	-1
LAGO	0	-2	-5	-6	-8	-7	91	-5	-5	-5	-4	-4	-2	-3	-1	-2	-1	-2
MOUSSE	0	0	4	4	5	7	-4	-4	-3	5	-12	-4	5	-5	3	-5	2	-3
MOUSSE	0	0	0	-5	-1	1	-1	1	2	7	-1	0	0	0	0	-2	-2	-1

COREXIT 9527	PERCENTAGE CHANGE BY CARBON NUMBER																	
OIL	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
ASMB	0	0	10	8	9	10	-10	9	7	4	-3	6	4	-13	0	-17	0	-7
ASMB	0	5	1	-3	-2	-3	-10	-2	-1	22	2	3	3	-5	-1	-6	-2	-1
HIBERNIA	0	0	0	0	0	-12	22	4	3	7	-5	-6	0	-6	0	-4	0	-1
LAGO	0	0	-5	-8	-8	-9	18	18	-7	33	-6	-6	-5	-4	-3	-2	-2	-1
MOUSSE	0	-1	-3	2	3	0	35	-1	-9	10	-5	-7	-5	-5	-3	-3	-2	-2
MOUSSE	0	0	0	-6	-6	-2	3	21	-4	3	-1	0	-4	-3	-1	-2	0	-1

ADGO	PERCENTAGE CHANGE BY CARBON NUMBER																	
DISPERSANT	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26
EN 700	0	0	5	7	3	2	-1	1	-16	4	0	5	0	-5	0	-5	0	-3
EN 700	0	0	2	1	-2	1	-1	-5	-21	18	2	10	0	0	0	-1	-1	-2
COREXIT 9527	0	0	19	0	13	16	-22	0	-28	-8	10	12	0	0	0	-9	0	-4
COREXIT 9527	0	0	34	0	17	21	-11	0	-27	0	-19	13	0	0	0	-13	0	-6